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ECBC-TR-499

GENERATION, SAMPLING, AND ANALYSIS FOR LOW-LEVEL GF (CYCLO-SARIN) VAPOR FOR INHALATION TOXICOLOGY STUDIES

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14. ABSTRACT
The generation, sampling, and analysis system used for low-level GB inhalation studies was modified to test the nerve agent GF. A saturator cell used in conjunction with an inhalation chamber generated low-level GF vapor at concentrations ranging from 0.004 - 0.05 mg/m^3. Additional testing with a syringe drive spray atomization system generated GF vapor concentrations from 0.7 - 2 mg/ m^3. This capability was important to determine sub-lethal effects (primarily miosis) for inhalation toxicology studies. In addition, the techniques successfully employed for this study would lay the foundation for testing low-level VX.

15. SUBJECT TERMS

GF	Agent generation	Saturator cell
Cyclohexyl methylphosphonofluoridate	Inhalation toxicology	Spray atomization
Low-level	Chemical agent	

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PREFACE

The work described in this report was authorized under Project No. 201400, Low Level Toxicology. This work was started in April 2002 and completed in April 2005. The experimental data are recorded in laboratory notebook nos. 01-0126 and 04-0146. The storage location for all the raw data and final report are in the Toxicology Archives, Aberdeen Proving Ground, MD.

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CONTENTS

FIGURES

TABLES

GENERATION, SAMPLING, AND ANALYSIS FOR LOW-LEVEL GF (CYCLO-SARIN) VAPOR FOR INHALATION TOXICOLOGY STUDIES

1. INTRODUCTION

Procedures for establishing the generation, sampling, and analysis methodologies for low-level agent inhalation studies began with the highest volatile nerve agent sarin (GB).[1,2] In these studies, stable GB vapor concentrations were established using a saturator cell generator in a 1000-L dynamic flow inhalation chamber. This exposure system generated a wide range of vapor concentrations extending from 0.0002 - 0.1 mg/m^3 GB. The dynamic range and stability demonstrated by this generation system for GB was tested with the less volatile agent GF.

In this study, the generation, sampling and analysis system used for GB was modified to generate stable low-level GF vapor concentrations. This would allow inhalation toxicity studies to determine low-level toxic effects, particularly miosis.

2. MATERIALS AND METHODS

2.1 Chemicals.

Munitions grade GF (lot # GF-S-6092-CTF-N-1) was distilled by the Agent Chemistry Team, U.S. Army Edgewood Chemical Biological Center (ECBC). Percent purity of the distillate from two separate NMR^{31}P determinations was 98.8 ± 0.5 wt % and 100.5 ± 0.7 wt %. Triethylphosphate (99.9% purity), obtained from Aldrich Chemicals (Milwaukee, WI) was used as the internal standard for the GF purity assay[3] (99.7%).

2.2 Chemical and Physical Properties.

Among the traditional nerve agents, GF has a volatility that lays between the most volatile agent, GB (~38 x more volatile than GF), and the least volatile agent, VX (~ 55x less volatile than GF). Pertinent physical and chemical data for vapor exposures of GF (Table 1) shows that the amount of GF vapor present at room temperature (548 mg/m^3) poses a significant inhalation hazard.[4,5]

Table 1. Physical and Chemical Data for GF[4,5]

Chemical Name	Cyclohexyl methylphosphono fluoridate	
CAS No.	329-99-7	
Molecular Formula and Weight	$C_7H_{14}FO_2P$	180.2 g/mol
Vapor Density Relative to Air	6.2	
Vapor Pressure @ 20 °C	0.0556 mm Hg	
Boiling Point and Volatility	228 °C,	548 mg/m^3 @ 20 °C 817 mg/m^3 @ 25 °C

2.3 GF Test Atmosphere System, Overview.

The vaporization system (syringe drive or saturator cell) was contained in a generator box, which in turn was connected to the inlet of a dynamic flow inhalation chamber (Figure 1). High vapor concentrations in the chamber (1 - 2 mg/m^3) were generated with a syringe drive/spray atomization system. Low vapor concentrations (0.004 - 0.10 mg/m^3) were generated using a saturator cell. The GF vapor was monitored in the chamber with sorbent tube sampling followed by thermal desorption and gas chromatographic (GC) analysis. A phosphorus analyzer also continuously monitored GF vapor at levels exceeding 0.004 mg/m^3.

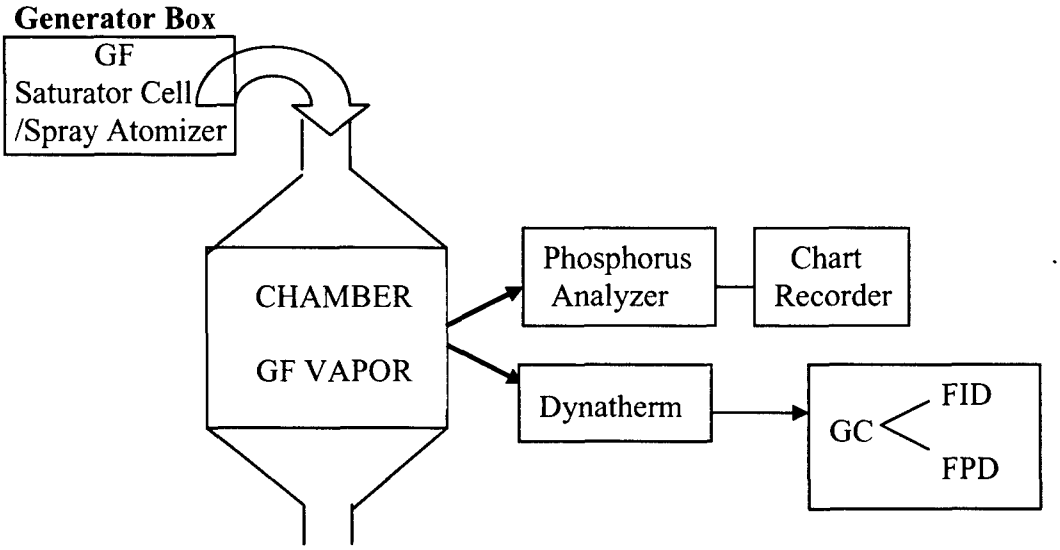

Figure 1. GF Inhalation Chamber and Monitoring Systems

2.4 Vapor Generation System.

2.4.1 Syringe Drive/Spray Atomization System.

Prior to chamber operation, the liquid agent was drawn into a gas-tight syringe (Hamilton, Reno, NV), then mounted onto a variable rate syringe drive (Model 22, Harvard Apparatus Inc., South Natick, MA). Once activated, the syringe drive delivered a constant flowrate of agent (microliter/minute) through a flexible plastic line (~ 8") into a spray atomization system (Spray Atomization Nozzle Series Stainless Steel (SS) 1/4 J, Spraying Systems Company, Wheaton IL). The atomizer was modified by inserting a syringe needle (SS 25 gauge 3") into the top of the sprayer to decrease the orifice size. As liquid agent entered through the top of the atomizer, compressed air (20 psi) entered through the side to atomize the liquid into fine droplets. These droplets quickly evaporated into GF vapor, which were then drawn down through the chamber.

2.4.2 Saturator Cell.

Saturated GF vapor streams were generated by flowing nitrogen carrier gas through a glass vessel (multi-pass saturator cell) containing liquid GF (Figure 2). The saturator cell (Glassblowers Company, Inc., Turnersville, NJ) consisted of a 100-mm long, 25-mm o.d. cylindrical glass tube with two (inlet, outlet) vertical 7-mm o.d. tubes connected at each end. The main body of the saturator cell contained a hollow ceramic cylinder [alundum® high purity fused alumina (Al_2O_3 - 90%), Saint-Gobain Ceramics & Plastics Inc., Worchester, MA], which served to increase the contact area between the liquid GF and the nitrogen. The saturator cell was fabricated to allow nitrogen to make three passes along the surface of the wetted ceramic cylinder before exiting the outlet arm of the glass cell. The cell body was also immersed in a constant temperature bath so that a combination of nitrogen flow and temperature could regulate the amount of GF vapor going into the inhalation chamber. In addition, the outlet arm of the glass cell was heated when the constant temperature bath was set above ambient temperature.

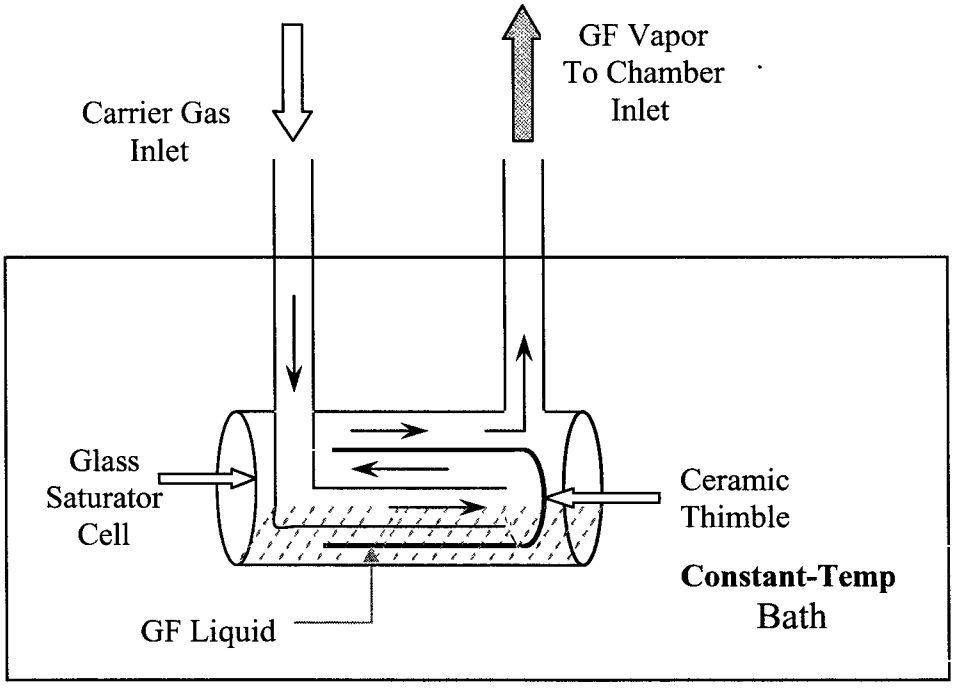

Figure 2. GF Vapor Generation via Saturator Cell

Typically, the saturator cell was loaded with 2-3 mL of liquid GF. Immediately after loading, a low nitrogen flowrate (1-2 mL/min) continuously flowed through the cell to maintain the integrity of the liquid GF. This allowed the saturator cell to be used as a generation source for approximately 1-2 weeks.

2.5 Inhalation Chamber.

The GF vapor was generated and monitored in a 1000 L dynamic airflow inhalation chamber. The Rochester style chamber was constructed of stainless steel with Plexiglas windows on each of its six sides. The interior of the exposure chamber was maintained under negative pressure (0.25" H_2O), which was monitored with a calibrated magnehelic (Dwyer, Michigan City, IN). A thermoanemometer, Model 8565 (Alnor, Skokie, IL), was used to monitor chamber airflow at the chamber outlet.

2.6 Sampling System.

2.6.1 Sorbent Tube System.

The automated solid sorbent tube sampling system consisted of four parts: (1) a sample line threaded within a heated (175 °C) sample transfer line; (2) a heated (175 °C) external switching valve; (3) a thermal desorption unit; and (4) a gas chromatograph (GC) (Figure 3). The silicosteel® sample line (1/16" o.d. x 0.004" i.d. x 6' length, Restek Corporation, Bellefonte, PA) extended from the middle of the chamber to an external sample valve. From the transfer line, the sample entered a heated 6-port gas-switching valve (UWP, Valco Instruments, Houston, TX). In the by-pass mode, GF vapor from the chamber continuously purged through the sample line and out to a charcoal filter. In the sample mode, the gas sample valve redirected GF vapors from the heated sample line to a Tenax® TA sorbent tube (20-35 mesh, 10 cm x 6 mm o.d.), which was located in the Dynatherm thermodesorption unit (ACEM-900, CDS, Oxford, PA). Temperature and flow programming within the Dynatherm desorbed GF from the sorbent tube directly onto the GC column (Restek Corporation, RTX-5, 30 m, 0.32 mm i.d., 0.5 mm thickness). Instrumental parameters for the GC and Dynatherm are listed in the Appendix.

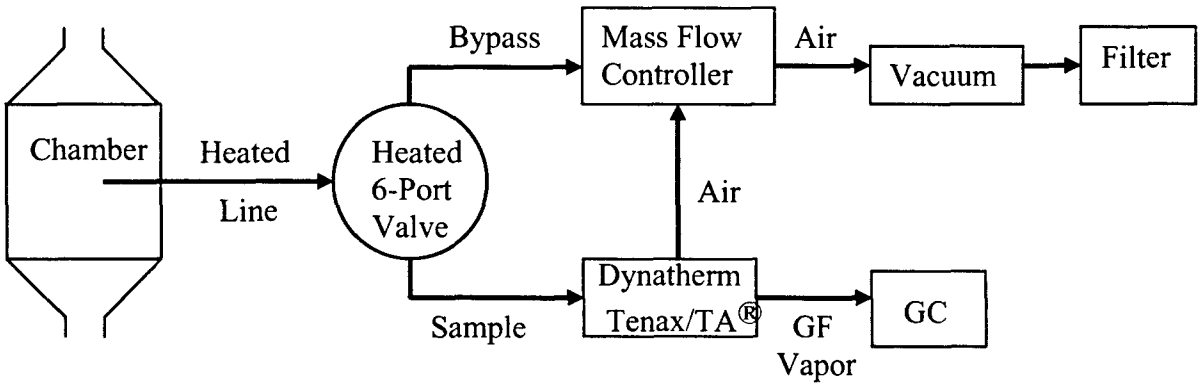

Figure 3. Automated Sorbent Sampling of GF Vapor from the Chamber

Sample flowrates for the sorbent tube systems were controlled with calibrated mass flow controllers (Matheson Gas Products, Montgomeryville, PA). Typical flowrates were approximately 100 sccm for the sorbent tubes. Flowrates were verified before and after

sampling by temporarily connecting a calibrated flowmeter ("DryCal", Bios International, Pompton Plains, NJ) in line to the sample stream.

The solid sorbent tube sampling system was calibrated by direct injection of external standards (GF/hexane - microgram/milliliter) into the heated sample line of the Dynatherm. In this way, injected GF standards were put through the same sampling and analysis stream as the chamber samples. A linear regression fit ($r^2 = 0.999$) of the standard data was used to compute for the GF concentration of each chamber sample.

2.6.2 Phosphorus Monitor (Hydrogen Flame Emission Detection, HYFED).

The GF levels in the chamber were continuously monitored with a phosphorus analyzer HYFED, Model PH262 (Columbia Scientific, Austin, TX). The analyzer output was recorded on a strip chart recorder, which showed the rise, equilibrium, and decay of the chamber vapor concentration during each experimental run. In addition, it gave a close approximation of the amount of GF (mg/m^3) in the chamber based on data (sorbent tube quantitation with HYFED response) from previous chamber runs.

2.7 Generation, Sampling, and Monitoring for GF Vapor.

The syringe drive/spray atomizer was used to generate GF vapor concentrations >0.6 mg/m^3. Syringe drive settings ranged from 0.7 - 1.75 µL/min with chamber flows of approximately 1,000 L/min to achieve the GF vapor concentrations. Once the spray atomizer was activated and the chamber had achieved equilibrium (t_{99}, the time in minutes it takes the chamber to achieve 99% of its vapor concentration), vapor samples were drawn and collected onto solid sorbent tubes for subsequent gas chromotograph-flame ionization detection (GC-FID) analysis. All sorbent tube samples were drawn intermittently at the rate of 0.1-.2 L/min for 3-5 min.

GF vapor concentrations less than 0.6 mg/m^3 were generated using the glass saturator cell. Four separate chamber runs (1-4 hr) were conducted to evaluate the generator performance at low GF vapor concentrations ranging from 0.004 – 0.05 mg/m^3. Changes of GF vapor concentrations were made primarily through adjustments in water bath temperature and carrier flow through the cell. Generator and chamber parameters used to achieve each concentration are listed in Table 2. All sorbent tube samples were drawn at the rate of 0.1-0.2 L/min for 1-5 min and quantified by gas chromatograph-flame phosphorus detection (GC-FPD).

2.8 GF Vapor and Analysis System.

A verification of the sampling and analysis system for GF vapor was conducted by comparing sorbent tube samples drawn directly from the chamber versus samples drawn through the heated line. Adjustments for the sample line temperature (≥170 °C), as well as

thermal desorption parameters (such as increased heating and vapor transfer times), were made to ensure complete transfer of GF vapor from the inhalation chamber to the GC.

Table 2. Generator and Chamber Parameters for GF Vapor (1-4 hr)

GF Vapor Actual (mg/m^3)	GF Vapor Nominal (mg/m^3)	N_2 Flow Through Cell (sccm)	Water Bath Temp (^{o} C)	Chamber Flow (SLPM)	Run Time (hr)
0.051	0.065	40	28.8	664	1
0.034	0.038	23	28.8	662	4
0.013	0.017	24.5	19.8	761	4
0.0036	0.0054	7.6	19.8	756	4

3. RESULTS

Vapor concentrations for GF were plotted over time for each chamber run. Each chamber run consisted of a series of measurements taken for a specific concentration and run time. A combination of runs were plotted together to examine the stability of each vapor generation system at different concentrations over time. Figure 4 summarizes the stability of the syringe drive-spray atomizer for three separate 3-hr chamber runs at the higher GF levels (0.7 - 2 mg/m^3). Figure 5 summarizes the stability and range of the saturator cell for four separate chamber runs (1-3 hr) at the low GF vapor levels (0.004 – 0.05 mg/m^3).

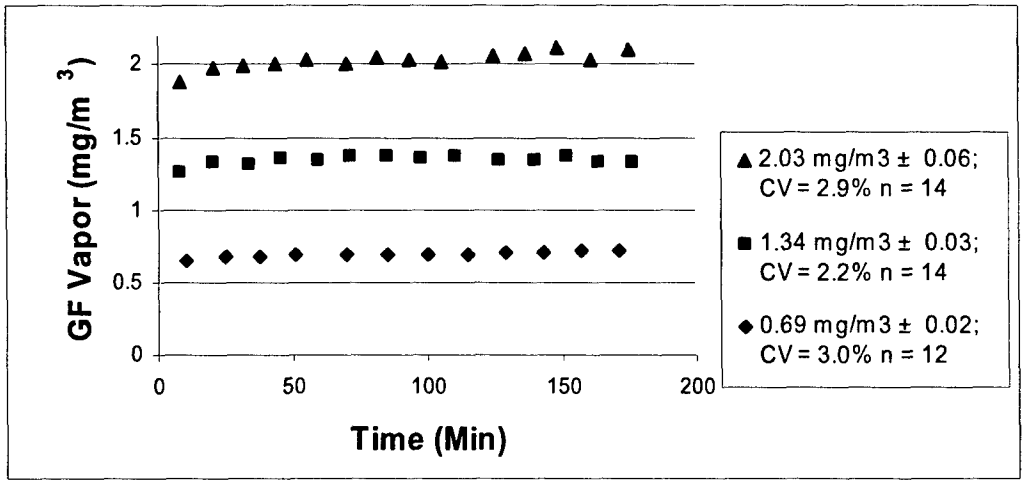

Figure 4. Spray Atomizer Generation of GF Vapor (High Range) for 3 hr

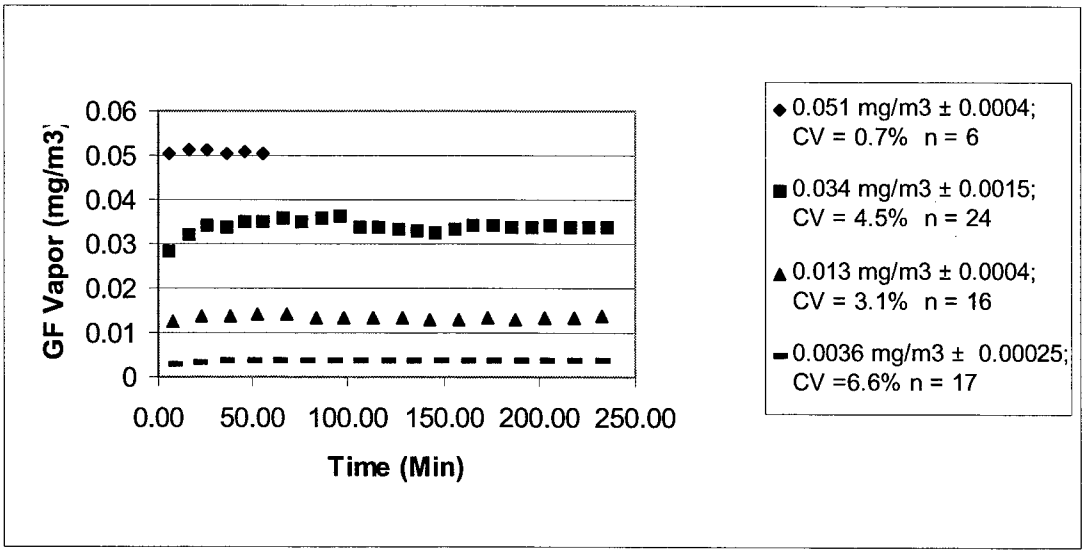

Figure 5. Stability of Saturator Cell to Generate Low-Level GF Vapor for 1-4 hr

4. DISCUSSION

4.1 Vapor Generators.

A summary of vapor generation techniques for the dissemination of CW agents has been described by Tevalt and Ong.[6] Typically these techniques have used a variety of liquid sparging, diffusion and/or metering devices to generate and maintain a steady vapor concentration in air. Previous generators used for GF inhalation studies in the 1940's and 50's consisted of either dispersion bubblers to spray the agent or bubblers containing the agent in a water bath with nitrogen flow.[6,7] Recent inhalation toxicity studies have successfully used a saturator cell to generate low-level GB vapor.[2,8]

4.2 Saturator Cell.

Vapor generation from the saturator cell followed the ideal gas law whereby:

$$PV = nRT \qquad (1)$$

where

P = Pressure (mm Hg)
R = Gas Constant
V = Volume (L)
T = Temperature (K)
n = g/mol

By rearranging the equation and substituting liters (L) for (V), we have:

$$g/L = PMW/RT \quad (2)$$

The vapor pressure (P) of GF can be computed using Antoine's equation (eq 3 and 4) and by applying the coefficients A = 8.15486, B = 2399.71, and C = 234.897 as determined by Tevalt et al.[5]

where

$$\text{Log10 } P = A - B/(C + \text{Temp } {}^{o}C) \quad (3)$$

or

$$P \text{ (mm Hg)} = 10 \text{ ^ } (A - B/(C + \text{Temp } {}^{o}C) \quad (4)$$

Thus, the concentration of GF vapor from the outlet of the saturator cell can be calculated from equation 5 as

$$\text{GF } \mu g/\text{min} = \frac{(P \text{ mm Hg})\ (180.2 \text{ g/mol GF})}{62.4\ \frac{(\text{mm Hg})\ (L)}{(\text{mole})\ (K)}\ (273.15 + {}^{o}C)\ K} \times (10^{6}\ \mu g/g) \times (\text{sccm/min} \times .001\ L/mL) \quad (5)$$

where

^{o}C = temperature of the water bath
sccm/min = carrier flow through the saturator cell.

The nominal chamber concentration can be calculated by dividing the rate of GF generated from the saturator cell (eq 5) by the chamber flow (SLPM) to obtain GF microgram/liter. However, other factors such as the deposition of GF vapor on the chamber walls affected the final vapor concentration.

4.3 Vapor Stability in the Chamber.

The syringe drive spray atomizer can typically generate GF vapor concentrations from 1 - 50 mg/m^3. This study examined the lower range of this generator at vapor concentrations ranging from 0.7 - 2 mg/m^3. Variations for three chamber runs ranged from 2 - 3 % for over a 3-hr period.

The saturator cell generated GF vapor concentrations ranging from 0.0036 - 0.05 mg/ m^3. Variations for four chamber runs ranged from 1 - 7 % for periods of 1 - 4 hr. Some of the variation was due to chamber conditioning or allowing the chamber enough time to attain equilibrium once a generator parameter (temperature or flow) was changed. Due to the lower volatility of GF, it was easier to generate the low vapor concentrationcompared to previous studies with GB.[2] Typically this range would be used to access inhalation toxicity for subclinical effects (i.e., EEG, blood serum changes, or tissue accumulation) and for extended (3 hr) miosis exposures.

4.4 Methodology Changes for GF versus GB.

Sampling differences between the GF and GB agent vapors were as follows:

- The GF was quantitatively sampled on sorbent tubes containing Tenax® TA with sample flowrates up to 0.21 L/min; whereas, GB flowrates were restricted up to 0.1 L/min with Tenax® TA. Higher flowrates (0.1 – 1 L/min) for GB required sorbent tubes containing a more retentive resin such as Tenax® TA (20-35 mesh)/HayeSep-D (60-80 mesh).

- The heated sample transfer line and the heated switching valve into the dynatherm required increased heating to prevent GF vapor loss. The sorbent tube collection temperature for GF was slightly higher (45 ^oC vs. 40 ^oC) compared to GB.

Analytical differences between the GF and GB agent vapors were as follows:

- The Dynatherm (sorbent tube) parameters required increased heating and vapor transfer times to ensure complete transfer of GF vapor from the sorbent tube to the GC.

- The GC column had a lower film thickness and higher temp profile to elute the GF peak at a retention time of 5 min.

Vaporization and Chamber vapor concentrations differences between GF and GB vapors were due to its lower vapor pressure. Low levels of GF vapor were easier to generate than GB.

5. CONCLUSIONS

This paper describes the techniques that were used for the generation, sampling and analysis of GF vapor particularly at low-levels are described in this report. The spray atomization system was an effective generator for the higher vapor concentrations (1-2 mg/m^3). The saturator cell generated low-level GF vapor ranging from 0.004-0.05 mg/m^3. Both generators produced stable vapor concentrations for an extended period of time with variations ranging from 1-7 %. In addition, the sampling and analysis system was a rapid and sensitive

method for performing low-level agent vapor studies. With adaptations, these techniques should be useful for testing less volatile agents such as VX.

LITERATURE CITED

1. Muse, W.T.; Anthony, J.S.; Buettner, L.C.; Durst, H.D.; Mioduszewski, R.J.; Thomson, S.A.; Crouse, C.L.; Crouse, L.C.B. *Comparison of Bubbler Versus Sorbent Tube Sampling For the Analysis of GB (Sarin) Vapor for Inhalation Toxicology*; ECBC-TR-202; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2002; UNCLASSIFIED Report (AD-A400 830).

2. Muse, W.T.; Thomson, S.A.; Crouse, C.L.; Matson, K.L. *Generation, Sampling and Analysis for Low-Level GB (Sarin) for Inhalation Toxicology Studies*; ECBC-TR-478; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2006; UNCLASSIFIED Report (AD-A448 866).

3. Brickhouse, M.D.; Rees, M.S.; O'Connor, R.J.; Durst, H.D. *Nuclear Magnetic Resonance (NMR) Analysis of Chemical Agents and Reaction Masses Produced by their Chemical Neutralization*; ERDEC-TR-449; U.S. Army Edgewood Research, Development and Engineering Center: Aberdeen Proving Ground, MD, 1997; UNCLASSIFIED Report (AD-A339 308).

4. Abercrombie, P.L. *Physical Property Data Review of Selected Chemical Agents and Related Compounds: Updating Field Manual 3-9 (FM 3-9)*; ECBC-TR-294; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2003; UNCLASSIFIED Report (AD-B294 480).

5. Tevault, D.E.; Buchanan, J.H.; Buettner, L.C.; Matson, K. *Vapor Pressure of Cyclohexyl Methylphosphono Fluoridate (GF)*; ECBC-TR-304; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2003; UNCLASSIFIED Report (AD-B292 165).

6. Tevault, D.E.; Ahearn, W.; Ong, K.Y.; Wasserman, M.B. *Vapor Generation Methods for Chemical Warfare Agents*; ECBC-TR-148; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2001, UNCLASSIFIED Report (AD-A389 503).

7. Skipper, H.E.; Silver, S.D. *Toxicity Determinations: Methods in Use in Medical Research Division, Edgewood Arsenal; CWS-FLM-1-4-2*; U.S. Army Chemical Warfare Center: Edgewood Arsenal, MD, 1943; UNCLASSIFIED Report (AD-E476 406).

8. Mioduszewski, R; Manthei, J.; Way, R.; Burnett, D.; Gaviola, B.; Muse, M.; Thomson, S.; Sommerville, D.; Crosier, R. *Low-Level Sarin Vapor Exposure in Rats: Effect of Exposure Concentration and Duration on Pupil Size*; ECBC-TR-235; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2002; UNCLASSIFIED REPORT (AD-A402 869).

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APPENDIX
GAS CHROMATOGRAPH AND THERMAL DESORPTION PARAMETERS
FOR GF ANALYSIS

GC/FPD Operation for Dynatherm

Gas chromatograph	Agilent 6890
Capillary column	RTX-5, 30m x 0.32mm i.d., x 0.5 mm film thickness
Column flow (He)	Velocity = 66 cm/sec; Head pres = 20.0 psi initial – 0.5 min, ramp @ 50 psi/min to 30 psi.
Detector flow (FPD)	100 mL/min (air); 75 mL/min (H_2); 15 mL/min (make-up He)
Detector temp (FPD)	250 °C
Col temperature program	60 °C (hold 0.5 min) to 175 °C @ 25 C°/min (run time: 5 min)

GC/FID Operation for Dynatherm

Same Chromatographic Parameters as above except:

Detector flow (FID)	450 mL/min (air); 40 mL/min (H_2); 45 mL/min (make-up He)
Detector temp (FID)	250 °C
Column flow (He)	Velocity = 66 cm/sec; Head pres = 20.0 psi initial - 2.0 min, ramp @ 20 psi/min to 50 psi.

Instrumental Parameters for Thermal Desorption

Model: Dynatherm (ACEM 900)

Temperature/Flow Program:

Tube Idle	45 °C	Tube Dry	1 min
Transfer Line	225 °C	Tube Heat	2 min
Tube Desorb	300 °C	Tube Cool	0 min
Trap Desorb	325 °C	Trap Heat	2 min
External Valve Temp	175 °C		
Internal Valve Temp	175 °C		
Purge Flow	50 sccm (He)		
Solid Sorbent	Tenax® TA (10 cm x 6 mm o.d.) (20-35 mesh)		

Sample Time:

External Sample	External
Standard Calibration through sample line	3-4 min
Chamber Sample	1-5 min